DETERMINATION OF THE KINETIC AND THERMODYNAMIC PROPERTIES OF BISULFITE ADDITION TO 4-NITROCINNAMALDEHYDE AND 4-DIMETHYLAMINOCINNAMALDEHYDE

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ABSTRACT

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The objective of this study is to compare the kinetic and thermodynamic properties of bisulfite addition to trans cinnamaldehyde and two trans-cinnamaldehyde derivatives in order to examine substituent effects on these properties. The equilibrium constants at pH 4.63 and at 25C of two para substituted derivatives were determined using a spectrophotometric technique. The equilibrium constants were determined to be 299 M^{-1} and 1340 M^{-1}, for 4-dimethylaminocinnamaldehyde and 4-nitrocinnamaldehyde respectively. Equilibrium constants were also determined at various temperatures, and changes in enthalpy and entropy were calculated to be: -39 KJ/mol and -84 J/molK for 4-dimethylaminocinnamaldehyde, and -18 KJ/mol and -.1 J/molK for 4-nitrocinnamaldehyde.

The forward rate constants were also determined, at pH 4.63 and 24.8C, by following absorbance of the aldehyde (upon addition of bisulfite) with respect to time, until equilibrium is reached. The forward rate constants for 4-dimethylaminocinnamaldehyde and 4-nitrocinnamaldehyde were 4.0 $M^{-1}s^{-1}$ and 42$M^{-1}s^{-1}$ respectively. By calculation, the reverse rate constants were 1.3 s^{-1} and 3.1 s^{-1} for 4-dimethylaminocinnamaldehyde and 4-nitrocinnamaldehyde respectively.

I would like to thank Professor Hull for giving me the opportunity to work with him on this project. His knowledge and guidance were invaluable to me during this work, and his understanding and patience have made this project very enjoyable.

Thank You,

Lisa Nerosi

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INTRODUCTION

In recent years the damaging effects of acid rain have encouraged the study of the atmospheric chemistry involved in its production. Increasing acidity of lakes, subsequent changes in aquatic life, and declining forests are evidence of the severity of this environmental threat. Studies have shown that excesses of SO_2 and NO_x, introduced to the atmosphere as pollutants, are the causes of acidity (1). These pollutants are released from oil and coal burning power plants and motor vehicle exhaust. Once in the atmosphere, the soluble gases are oxidized in either the gaseous or aqueous phase, and ultimately precipitated as acid rain. A complete understanding of the atmospheric chemistry involved is essential to finding a solution to this urgent dilemma.

It is primarily the oxidation of sulfur dioxide that concerns this project. SO_2 exists as three species in equilibrium: $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-}. These three species are collectively referred to as S(IV), since each contains the element sulfur in the plus four oxidation state. In the pH range of interest, that of cloudwater and rainwater, pH 2-6, the dominant S(IV) species is HSO_3^-, bisulfite ion (2).

The S(IV) species is oxidized to the S(VI) species in both the aqueous and gaseous phases. However, Finlayson-Pitts and Pitts have attributed about 90% of S(IV) oxidation to aqueous phase reactions (3). They also recognize hydrogen peroxide as the major oxidant in this phase. This is due to two factors. Oxidation by hydrogen peroxide is a rapid reaction, and hydrogen peroxide is highly soluble relative to other possible oxidants. Thus, even a low concentration of peroxide in the gas phase gives rise to considerable amounts in the aqueous phase. Penkett, et al. have also found that at pH less than 5.6, H_2O_2 is the most important oxidizing reagent and the oxidation by H_2O_2 is virtually pH independent (in contrast to rections with other possible oxidants) (4). The relevant equations follow.

$$\underset{}{SO_2\,(g)} \xrightarrow{H_2O} \underset{S(IV)}{HSO_3\,(aq)} + H^+\,(aq)$$

$$S(IV) + H_2O_2 \xrightarrow{aq} S(VI) + H_2O$$

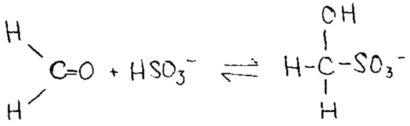
One way to inhibit the production of S(VI) is to limit the amount of available S(IV). There is evidence of formation of a formaldehyde-bisulfite adduct, called hydroxymethane sulfonate, which ties up S(IV) and delays its oxidation. In view of the significant levels of carbonyl compounds found in the atmosphere, other adducts (produced by the reaction between bisulfite and higher aldehydes and some unhindered ketones) could play an important role in the chemistry of acid rain. Also, since these carbonyl compounds are released as pollutants, their occurance is likely to coincide with that of S(IV).

Several studies show that carbonyl compounds, especially aldehydes and ketones, are indeed present in the atmosphere (5). Schulam and Hull measured aldehyde levels in rural New York to determine a "backround concentration" (6). Formaldehyde concentrations ranged from 0.8 ppb to 2.6 ppb, and aldehyde concentrations ranged from 0.2 ppb to 0.8 ppb. In urban Schenectady, New York, the same study found much higher formaldehyde concentrations (1-31 ppb), suggesting pollutants as a source of carbonyl compounds in the atmosphere. The study also notes that daily variations in urban aldehyde concentrations coincide with traffic patterns.

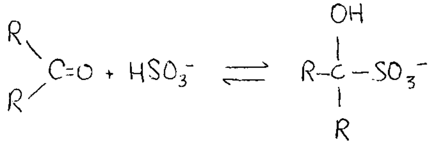
Grosjean has recorded concentrations of aldehydes in the Los Angeles area during intense smog episodes (7). In addition to formaldehyde levels as high as 48 ppb and acetaldehyde levels as high as 35 ppb, several other carbonyl compounds were confirmed to be present in significant amounts. Measurements of propanal, butanal, 2-butanone, and benzaldehyde were made. Grosjean's measurements made in Claremont, 50 km east of L.A., showed that carbonyl compound concentrations were at maxima when smog fronts from L.A. hit Claremont. Again, there is a strong suggestion that pollution from burning hydrocarbons is a major source of carbonyl compounds in the atmosphere. Munger has found similar support for this idea (8).

As previously stated, these carbonyls can form adducts with S(IV) compounds and thus decrease the amount of S(IV) available for conversion to S(VI). Richards, et al, found that S(IV) levels were more than 100 times the expected concentration at given conditions (9). In the presence of formaldehyde, hydrogen peroxide and S(IV) were found to coexist, even when hydrogen peroxide was in excess. It was concluded that oxidation was inhibited by adduct formation and subsequent stabilization of the reduced sulfur species. One third of the total measured S(IV) was found in the form of hydroxymethane sulfonate, HMSA, the product of formaldehyde-bisulfite adduct formation. The rest of the S(IV) must be tied up in adducts of other carbonyl compounds.

The reaction of formaldehyde and bisulfite is the simplest example of adduct formation. The reaction proceeds as follows.



The equilibrium constant for this reaction is reported to be 85,000 M^{-1} at pH 5.0 (10). There is a corresponding reaction known to take place between bisulfite and higher aldehydes and some unhindered ketones (3).



According to Lowry, et al, these reactions are more favorable with aldehydes than ketones, and the equilibrium constants decrease with higher aldehydes (11). Munger, et al, concluded that the adduct formation is most favorable at temperatures around 0C, pH 3-6, and high S(IV) concentrations (8).

Carbonyl-bisulfite adducts are important to the overall scheme of atmospheric chemistry. The reaction to form adducts competes for S(IV) with the oxidation reaction. The former reaction results in the ultimate production of one hydrogen ion, while the latter reaction produces two. There may be a minor effect on the acidity of rainwater. However, the more important consequence is that the production of the hydrogen ion by reaction of the adduct is delayed until the cloudwater evaporates. Thus, sulfur pollutants may be carried as S(IV) (via adduct formation) for some distance from the source before it is oxidized to produce acid.

Although the formation of adduct is slow relative to the oxidation process (3), aldehydes and ketones can still compete for S(IV) because the adducts formed are very stable. The slow rate of dissociation of the adduct can lead to a build up of the adduct (and thus S(IV)) (8). In contrast, the oxidation reaction involves an irreversible reaction of S(IV) to S(VI).

The extent to which carbonyl-bisulfite adducts can affect S(IV) chemistry depends on the equilibrium constant and kinetics of the particular adduct formation reaction. Therefore it is important to study the thermodynamics and kinetics of these reactions and the factors that affect them. It is the purpose of this study to explore the effects of substituents on aromatic aldehydes on rates and extents of adduct formation upon addition of bisulfite.

In a study similar to this one, Young and Jencks studied substituent effects in the reactions of substituted acetophenones with bisulfite (12). The equilibrium constants and rate constants they found (at 25C and ionic strength=1.0) are tabulated below.

Constants for the Reaction of Bisulfite with Substituted Acetophenones (12)

substituent	K(M^-1)	k(M^-1s^-1)
p-OCH3	[illegible]	23
p-CH3	3	46
H	5.5	77
p-Cl	8	192
m-Br	16	384
p-NO2	34	800

The results above can be used to predict the effects of similar substituents used in this research project.

This study will concentrate on bisulfite addition to trans-cinnamaldehyde and two of its derivatives, in order to examine the inductive effects of the substituents on the kinetics and thermodynamics of the reaction. The trans-cinnamaldehyde derivatives are 4-dimethylaminocinnamaldehyde (para substituted with an electron donating group, $-N(CH_3)_2$) an nitrocinnamaldehyde (para substituted with an electron withdrawing group, $-NO_2$). Based on the results of the Young and Jencks study, one would expect to observe a slight decrease in the equilibrium and rate constants for the bisulfite addition to 4-dimethylaminocinnamaldehyde relative to those of the unsubstituted trans-cinnamaldehyde. Conversely, since the electron withdrawing substituent can facilitate the acceptance of the negatively charged bisulfite ion by the carbonyl carbon, the reaction with 4-nitrocinnamaldehyde should have a faster rate, and a larger equilibrium constant than the reaction with trans-cinnamaldehyde

Trans-cinnamaldehyde is the aldehyde of choice for several reasons. This aldehyde lends itself easily to the spectrophotometric method of analysis used. Its high extinction coefficient, 25,000, makes it possible to work with low aldehyde concentrations since the absorbance is equal to the product of the extinction coefficient times the concentration of aldehyde. Trans-cinnamldehyde and its derivatives exhibit maximum absorbance at convenient wavelengths, at which there is no interference due to absorbance by bisulfite, acetate buffer, or optics. In order to study the electronic effects of a substituent, it must be located far enough from the reaction center that it is reasonable to assume that there are no steric effects operating. If a substituent is located too far from the reaction center its electronic effects may be diminished or may not be observed at all. The para substituents in this study are far enough from the carbonyl carbon not to affect the reaction sterically. However, due to the extensive conjugation of trans-cinnamaldehyde the substituents still have an electronic effect on the reaction. Another reason trans-cinnamaldehyde was chosen is that the bisulfite addition to this aldehyde is slow enough to allow several absorbance measurements before the reaction reaches equilibrium. Thus it is possible to determine the forward and reverse rate constants for the reaction. L.LeTarte has determined the equilibrium constant for bisulfite addition to trans-cinnamaldehyde to be 1030 M^{-1}, and the forward rate constant to be 24.3 $M^{-1}s^{-1}$, and by calculation, the reverse rate constant is 2.4 X $10^{-2}s^{-1}$ (13).

The method employed in this project is the same as that used by LeTarte (13). It is a variation on the procedure outlined by Kokesh and Hall (14). Bisulfite addition to the aldehyde is monitored with respect to time on a UV/VIS spectrophotometer in order to determine the rate constants for the reaction. The equilibrium constant is determined by following the absorbance at equilibrium after each of a series of bisulfite additions. The measurements are made based on two assumptions. It is assumed that there is no interference with absorbance due to bisulfite or buffer. Also, it is assumed that the aldehyde absorbs at the wavelength used while the adduct does not.

The absorbance at any time is related to the concentration of unreacted aldehyde (and adduct) using Beer's Law. Thus it is important to make sure the aldehyde adheres to Beer's Law. To check this, a plot of absorbance against aldehyde concentration is made , and a linear relationship is taken as proof of adherence to Beer's Law.

The derivations for the equations for the equilibrium constant, K_{eq}, and the forward rate constant, k_1, and the reverse rate constant, k_{-1}, can be found in LeTarte's thesis (13). K_{eq} is calculated from a plot of the following equation:

$$1/A = \{K_{eq}/E\,[C]_T\}\,[S] + 1/E[C]_T$$

where A is the absorbance of the aldehyde at equilibrium, E is the extinction coefficient, $[C]_T$ is the initial aldehyde concentration and [S] is the concentration of added bisulfite. The equilibrium constant is obtained by dividing the slope by the intercept.

The forward rate constant, k_1, is calculated from the rate constant observed when bisulfite is in excess (creating a psuedo first order reaction by making bisulfite concentration essentially constant), k', using the following equations:

$$k' = -\{\text{slope } (A_o - A_{inf})\} / A_o$$

$$k_1 = k' / [HSO_3^-]$$

where A_o is the initial absorbance and A_{inf} is the absorbance after reaching equilibrium, and the slope is the slope of a plot of ln ($A-A_{inf}$) vs. time. A plot of k' vs. $[HSO_3^-]$ yields a slope equivalent to the value of k_1. The reverse rate constant can be calculated from the experimental values of K_{eq} and k_1:

$$k_{-1} = k_1 / K_{eq} .$$

EXPERIMENTAL

PREPARATION OF SOLUTIONS

Buffer:

All bisulfite addition reactions were carried out in a buffered solution with pH 4.63 to ensure that the dominant S(IV) species present was HSO_3-. A 1.0 M, 1:1 acetic acid/sodium acetate buffer , with pH corrected to 4.63, and an ionic strength of 1.0, was used. One mole of sodium acetate was weighed directly into a 1 liter volumetric flask, and one mole of acetic acid was pipetted into the same flask, and this was diluted to 1 liter with deionized water. The ph was adjusted with NaOH or HCl just prior to reaching the one liter mark with water. This buffer did not absorb strongly at the wavelengths of interest in this experiment.

Aldehyde solutions:

Aldehyde stock solutions on the order of 10^{-2} M were prepared for trans-cinnamaldehyde, 4-nitrocinnamaldehyde, and 4-dimethylaminocinnamaldehyde. The aldehyde compounds were weighed directly into 10 ml volumetric flasks and then diluted to 10 ml with 100% ethanol. Trans-cinnamaldehyde is available as a liquid, so it was distilled to improve the purity of the stock solution prepared from it. The two cinnamaldehyde derivatives were available as solids. The purity of each of these solutions was confirmed by NMR analysis. Calibration curves were made for each aldehyde in order to check for adherence to Beer's Law, and to determine their extinction coefficients in the acetate buffer. Once prepared, these aldehyde solutions were stored under nitrogen, in brown glass bottles, at -4C. These solutions were replaced every four weeks.

Sodium Bisulfite:

A stock solution of approximately 0.8 M was prepared by weighing the sodium bisulfite directly into a 500 ml volumetric flask and diluting to 500 ml with deionized water. The stock solution was titrated with a standard iodine solution to determine its exact molarity. The concentration of this stock solution changed very little over the course of several months. However, stock solutions of approximately 8 X 10 $^{-2}$ M and 8 X 10^{-3} M were needed in order to make a bisulfite addition of reasonably measurable volume. These diluted stock solutions were very susceptible to changes in concentration due to oxidation of S(IV) to S(VI). It was thus necessary to prepare these solutions before each set of runs.

INSTRUMENTATION

A Perkin-Elmer Lambda 3B spectrophotometer interfaced with a Perkin-Elmer 3600 microcomputer was used to measure absorbances in the UV/VIS region. The data for the determination of the forward rate constant was collected using a program called KINS. The KINS program measured the absorbance of the solution in the sample cell at data intervals of one second or one half second, for a period of time programmed (usually fifteen minutes). The program could output the data as digits, or in the form of a graph. All measurements were taken using one cm absorption cells.

The temperature in the cell compartment was maintained using a Neslab Endcool RT-9 refrigerated circulating water bath. An Omega 871 thermometer was used to take temperature readings. pH readings were made using an Orion 701A digital ionalyzer.

METHOD

Determination of equilibrium constant:

The absorbance of the aldehyde in solution was measured initially and after a series of bisulfite additions. Three ml of buffer was pipetted into a reference cell and a sample cell. For 4-dimethylaminocinnamaldehyde, several microliters of .0280 M stock solution were injected into the sample cell using a 1-10 µL syringe. The range of initial aldehyde concentrations in the cell was 1.54×10^{-5} to 2.46×10^{-5} M. The initial absorbance at 399nm was read directly off the instrument, and a spectrum from 500 to 190 nm was recorded as a computer file. A series of 10 µL aliquots of .08069 M bisulfite solution were injected, using a 10-50 µL syringe, into both the reference and sample cells. A total of 60 µL of bisulfite was added, corresponding to bisulfite concentrations in the range of 0 to 1.62×10^{-3} M in the cells. After each bisulfite addition, the cell was shaken, and allowed fifteen minutes in a water bath to reach equilibrium (equilibrium was later determined to be established after about three minutes), before the absorbance was read directly off the instrument. After the final bisulfite addition, another spectrum was taken.

The work with 4-nitrocinnamaldehyde was done as described above except that the range of initial aldehyde concentration in the sample cell was 1.66×10^{-5} M to 4.29×10^{-5} M, and the bisulfite concentration in both cells varied from 0 to 1.62×10^{-4} M, and direct absorbance readings were made at 308 nm. It is important in both cases that the buffer and bisulfite be added to the reference cell (as well as the sample cell) in order to cancel out any absorbance due to these solutions. Also, the sample cannot be allowed to reach equilibrium in the closed cell compartment because prolonged exposure to the light causes photolysis of the aldehyde sample. Since the equilibrium constant is temperature dependent, it is best to allow the cell to reach equilibrium in the water bath, and return it to the cell compartment afterward for the absorbance measurement.

Determination of Rate Constants

The initial concentration of aldehyde is measured and then one bisulfite addition is made and the absorbance is monitored with respect to time while the solution in the sample cell establishes equilibrium. Three ml of buffer are pipetted into each of the absorbance cells, and several µL of aldehyde stock solution are injected (resulting in cell concentrations of approximately 4 X 10^{-5} M aldehyde solutions) into the sample cell. The time drive program and a stop watch are simultaneously started when the cells are placed in the compartment (there is a 12.0 second delay from the time the start command is given and the time the program actually starts recording data which must be corrected later). Once the display on the computer shows a steady initial absorbance at the wavelength of interest, the reference cell is removed and bisulfite (resulting in cell concentrations of 1.34 X 10^{-3} M HSO_3^- for work with 4-dimethylaminocinnamaldehyde , and 1.62 X 10^{-4} M HSO_3- for work with 4-nitrocinnamaldehyde) is added to it. An equal addition of bisulfite is then made to the sample cell. The stopwatch is stopped at the exact time of bisulfite addition so that times recorded by the database can be corrected and absorbance readings will correspond to actual time passed since the addition of bisulfite. This is done by taking the time recorded by the database, adding 12.0 seconds (to compensate for the time passed between initiation of the program and actual collection of data by the program), and subtracting the time recorded on the stopwatch (the time the program was running before bisulfite addition). The time thus calculated is t_0, the time of bisulfite addition. (Note this complicated method of calculating t_0 results because it was not discovered until later that the computer program did not collect data until 12 seconds after the program was started. Starting the stopwatch when the program starts data collection, instead of when the program is initiated, will simplify the calculation of t_0.) Once the bisulfite is added, the cell is quickly inverted to mix the solution inside and returned to the cell compartment in order to monitor as much of the decrease in absorbance as possible. Absorbance was measured every 0.5 seconds for about fifteen minutes. Since the reaction comes to equilibrium well before five minutes (at 25C), the constant absorbance at the end of the run is taken as the absorbance at equilibrium, or at infinity.

RESULTS

4-DIMETHYLAMINOCINNAMALDEHYDE

A literature value for the extinction coefficient of 4-dimethylaminocinnamaldehyde, DMACA, in buffer ,was not found. As a first approximation, it was assumed to be nearly that of trans-cinnamaldehyde, which is 25,400 in buffer Using this value for the extinction coefficient,E, and Beer's Law (Abs.=Eb*conc., where cell length,b,=1cm), a range of aldehyde concentrations which would produce a range in absorbance from 0 to 1 absorbance unit was calculated. A scan from 900 nm to 190 nm showed that the wavelength of maximum absorbance was at 399 nm. The wavelength of maximum absorbance for trans-cinnamaldehyde in the same buffer was 291 nm.

The actual absorbance measurements (at 399 nm) from these DMACA solutions in buffer are plotted against the concentration of DMACA in Figure 1. The correlation coefficient for the line produce is one, indicating that the aldehyde does follow Beer's Law. Also, the slope is equal to the real extinction coefficient of DMACA in acetate buffer; the value is 26,000. Notice that this value is very close to that of trans-cinnamaldehyde, as expected, since the conjugation in both aldehydes is similar.

The extinction coefficient obtained above was then used to determine what initial DMACA concentrations should be used to give an initial absorbances of approximately 1, .6, and .4, in three separate runs. The initial concentrations of DMACA in runs one through three were 3.46 X 10^{-5} M, 2.31 X 10^{-5}M, and 1.65 X 10^{-5}M. In each run, 10 microliter aliquots of .08069 M bisulfite solution were added, resulting in a range of bisulfite concentrations from 0 to 1.62 X 10^{-3} M. However, the first addition alone resulted in a bisulfite concentration (2.69 X 10^{-4}M) in excess of carbonyl concentration. It is necessary that bisulfite be in

Figure 1 Absorbance vs [DMACA] in Buffer

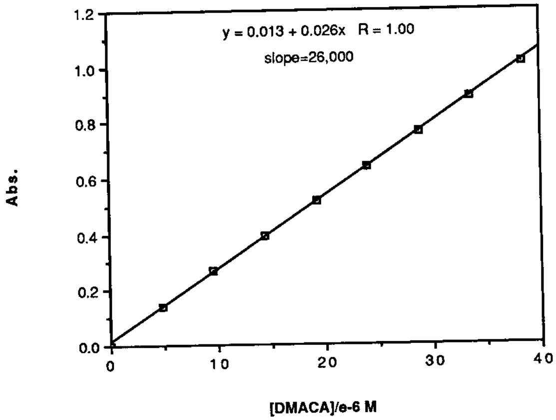
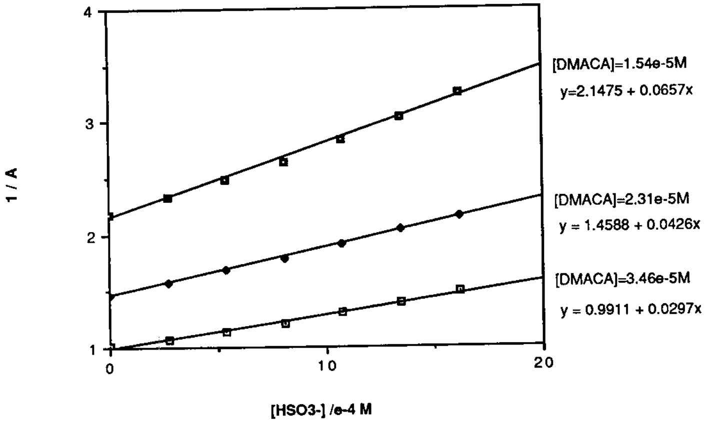


Figure 2
1/A vs [HSO3-],Varying [DMACA]o



excess in order to use the expression for the equilibrium constant derived by LeTarte (13).

Figure 2 shows a plot of 1/Absorbance vs. [bisulfite] for each of the three runs. In each case, the equilibrium constant was calculated by dividing the slope by the intercept. The results tabulated in Table 2 show that the equilibrium constant is independent of carbonyl concentration. The average equilibrium constant for bisulfite addition to DMACA, at 25.5 C, was 299 ± 7 M^{-1}.

Table 2 K_{eq} for Bisulfite Addition to DMACA
(temperature=25.5C)

Run	$[DMACA]_0$/M	K_{eq}/M^{-1}
1	3.46e-5	300
2	2.31e-5	292
3	1.54e-5	306
ave		299 ±7

The equilibrium constant is temperature dependent, and plotting $\ln(K_{eq})$ vs. 1/T allows a determination of the change in enthalpy,ΔH° and the change in entropy,ΔS° for the reaction. Figure 3 is a plot of 1/A vs. $[HSO_3^-]$ for five runs, varying temperature. In each run the initial concentration of DMACA is 3.46 X 10^{-5}M. Again, the slopes are divided by the intercepts to obtain the equilibrium constants. The results in Table 3 show that the equilibrium constants increase as the temperature is decreased.

Figure 3
1/A vs.[HSO3-], Varying Temperature for DMACA

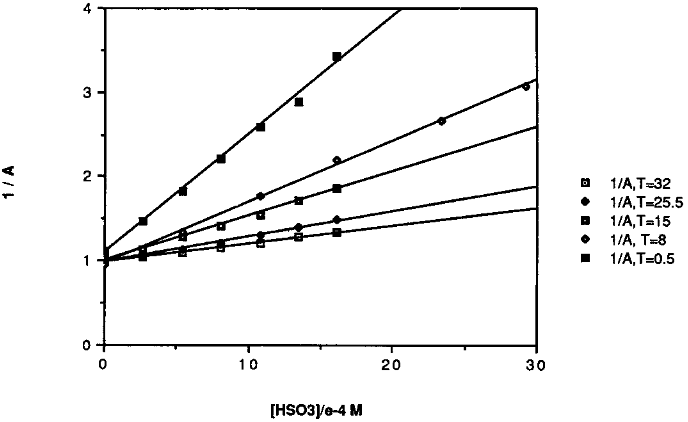


Figure 4
ln Keq vs. 1/T, for DMACA

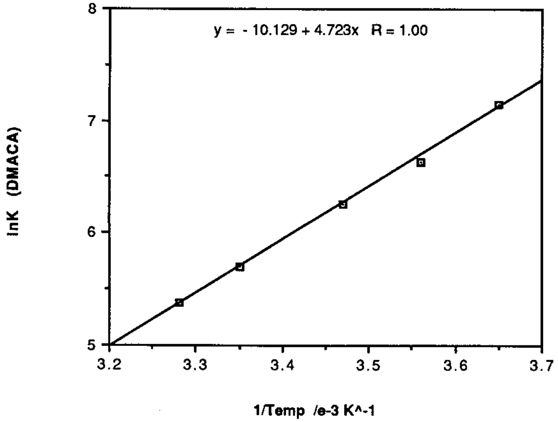


Table 3. K_{eq} for Bisulfite Addition to DMACA
([DMACA]$_0$= 3.46e-5M)

Run	Temp/C	K_{eq}/M^{-1}
1	32	215
2	25.5	300
3	15.0	524
4	8.0	757
5	0.5	1280

The ln(K_{eq}) vs 1/T is plotted in Figure 4. The slope and intercept are used to calculate H and S for bisulfite addition to DMACA using these relationships:

$$H = -slope*R \quad \text{and} \quad S = intercept*R$$

where R=gas constant=8.31441J/molK. H was calculated to be -39 KJ/mol, and S was calculated to be -84 J/molK.

The forward and reverse rate constants were also determined for bisulfite addition to DMACA. The data was collected as described in the experimental section. Figures 5-7 show plots of ln(A-A_{inf}) vs. time for three runs. The initial concentration of DMACA is 3.51 X 10^{-5} M for each run, and the temperature is 24.8C for each run, while the concentration of bisulfite added is varied. **k'** for each run is calculated from the plots in Figures 5-7, as described in the introduction. Table 4 summarizes the conditions used and the k' values obtained.

Figure 5 ln(A-Ainf) vs. Time, for DMACA
[HSO3-]=6.72 e-4 M

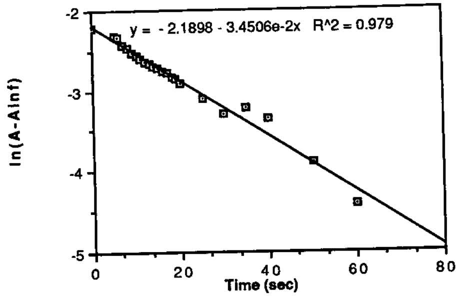


Figure 6 ln(A-Ainf) vs. Time, for DMACA
[HSO3-]=1.34 e-3 M

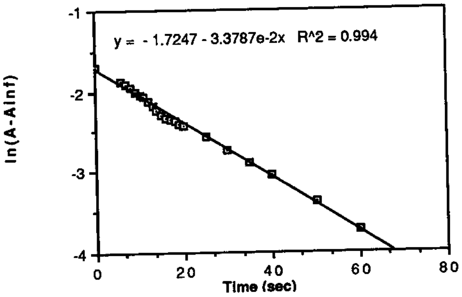


Figure 7 ln(A-Ainf) vs. Time, for DMACA
[HSO3-]=2.56 e-3 M

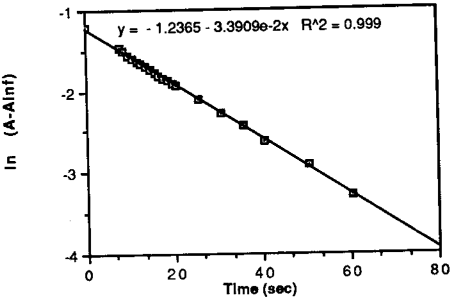


Table 4 Summary of Conditions Used, and k' Values Obtained for Bisulfite Addition to DMACA @ 24.8C

Figure	[DMACA](M)	$[HSO_3^-](M)$	k' (s^{-1})
5	3.51e-5	6.72e-4	3.83e-3
6	3.51e-5	1.34e-3	6.76e-3
7	3.51e-5	2.56e-3	1.14e-2

The values of k' were plotted against the bisulfite concentration in Figure 8. The forward rate constant, k_1, is taken as the slope of this plot (since k' = $k_1[HSO_3^-]$), as described in the introduction. Thus the forward rate constant for bisulfite addition to DMACA was determined to be 4.0 $M^{-1}s^{-1}$, and by calculation, the reverse rate constant was 1.3×10^{-2} s^{-1}.

4-NITROCINNAMALDEHYDE

The results for bisulfite addition to 4-nitrocinnamaldehyde, FNCA, were obtained in the same manner as described above for the reaction with DMACA. An absorbance spectrum of FNCA showed that the wavelength of maximum absorbance was 308 nm. All subsequent absorbance readings were thus made at this wavelength. A plot of absorbance vs. FNCA concentration in buffer is shown in Figure 9. The linear relationship is proof that FNCA adheres to Beer's Law, and the slope is equal to the extinction coefficient of FNCA in buffer. The value for E obtained is 23,190, similar to that of trans-cinnamaldehyde.

The equilibrium constant for bisulfite addition to FNCA was determined at various initial concentrations of FNCA to check that the constant was independent of carbonyl concentration. Once again, it was necessary that bisulfite be present in excess. However, it was discovered that using bisulfite

Figure 8
k'1 vs [HSO3-], for DMACA

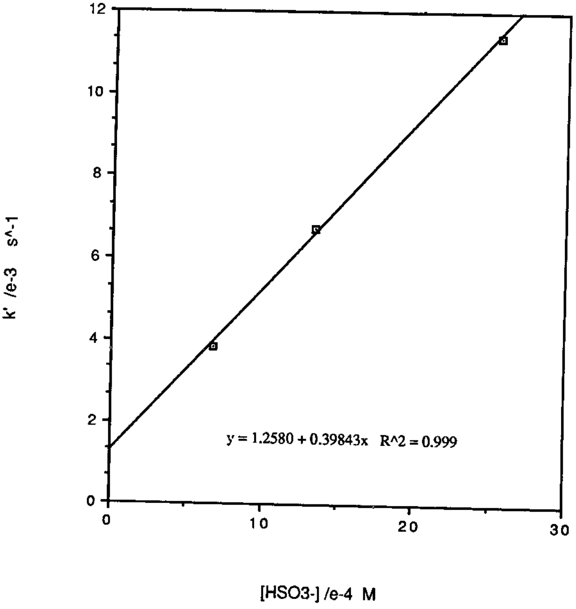


Figure 9
Absorbance vs [FNCA] in Buffer

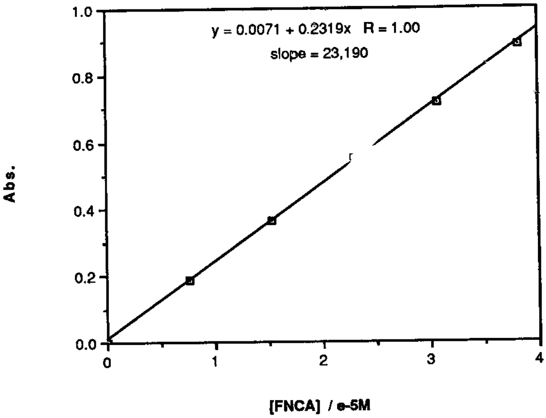
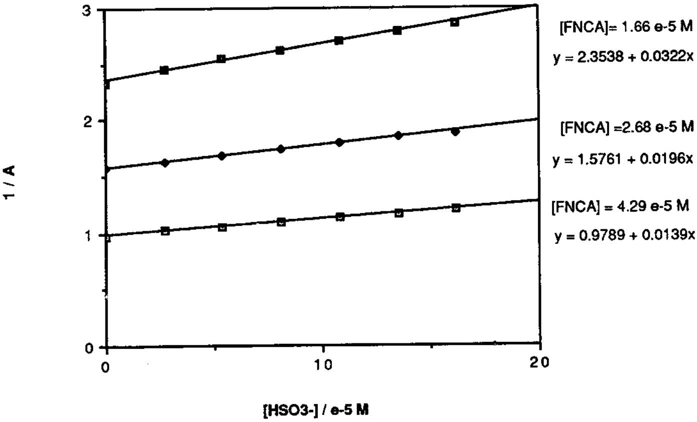


Figure 10
1/A vs [HSO3-],Varying [FNCA]o



concentrations on the order of 10^{-3} M (as used in the reaction with DMACA) did not result in a linear plot of 1/A vs. [bisulfite]. The reaction with FNCA is so favorable that bisulfite concentrations had to be decreased by a factor of ten. Thus 10 microliter aliquots of .008069 M HSO_3^- were added, resulting in bisulfite concentrations ranging from 0 to 1.62 X 10^{-4}M. In most runs, only after the second aliquot of bisulfite was added was the bisulfite in excess of carbonyl concentration.

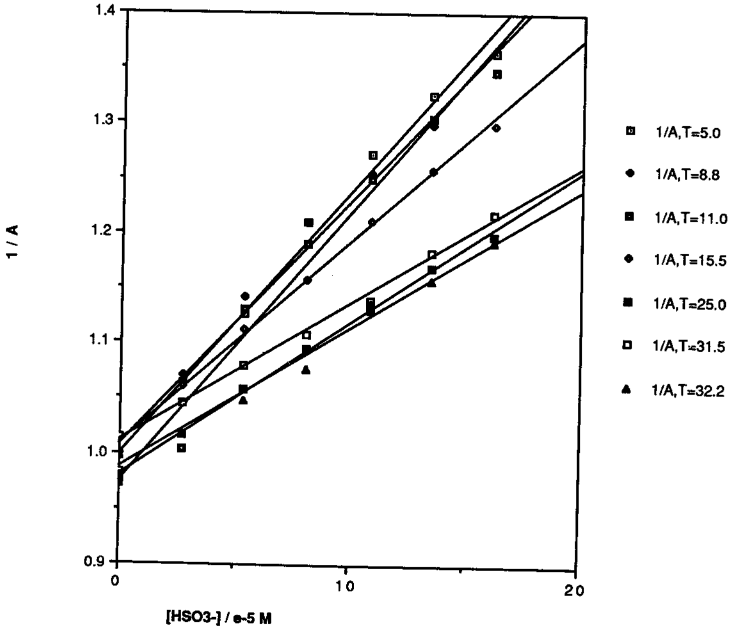
The initial FNCA concentrations for the three runs were : 4.26 X 10^{-5}M, 2.68 X 10^{-5}M, and 1.69 X 10^{-5}M. The temperature was 25C for all three runs. Figure 10 shows a plot of 1/A vs. [bisulfite] for each of the three runs. In each case, the equilibrium constant was calculated by dividing the slope by the intercept. The results listed in Table 5 show that the equilibrium constant, K_{eq}, is independent of carbonyl concentration. The average equilibrium constant at 25C is 1,340± 90 M^{-1}.

Table 5 K_{eq} for Bisulfite Addition to FNCA
(temperature=25C)

Run	$[FNCA]_0/M$	K_{eq}/M^{-1}
1	4.29e-5	1,420
2	2.68e-5	1,240
3	1.66e-5	1,370
ave		1,340±90

In order to determine ΔH° and ΔS° for the reaction, the equilibrium constants at various temperatures were obtained. It was found that below about 5C, it was not possible to get a constant absorbance reading. Figure 11 shows a plot of 1/A vs. $[HSO_3^-]$ for seven runs, varying temperature. In each run, the

Figure 11 FNCA
1/A vs. [HSO3-], Varying Temperature



initial concentration of FNCA is 4.29 X 10^{-5}M. The results in Table 6 show that the equilibrium constants increase as temperature is decreased.

Table 6 K_{eq} for Bisulfite Addition to FNCA
($[FNCA]_0$=4.29e-5M)

Run	Temp/C	K_{eq}/M^{-1}
1	5.0	2.41e+3
2	8.8	2.20e+3
3	11.0	2.51e+3
4	15.5	1.83e+3
5	25.0	1.42e+3
6	31.5	1.28e+3
7	32.2	1.28e+3

The ln(K_{eq}) vs. 1/T is plotted in Figure 12. From the plot, $\Delta H^{\circ}$was calculated to be -18 KJ/mol, and $\Delta S^{\circ}$was calculated to be -.13 J/molK.

The forward and reverse rate constants were also determined for FNCA. The data was collected as described in the experimental section. Figures 13-15 show plots of ln(A-A_{inf}) vs. time for three runs, each with a different concentration of added bisulfite. In each run the temperature is 24.8C. and the initial concentration of FNCA is 4.29 X 10^{-5} M. Table 7 summarizes the conditions used and the k' values obtained.

Table 7 Summary of Conditions Used and k' Values Obtained for Bisulfite Addition to FNCA @ 24.8C

Figure	[FNCA](M)	$[HSO_3^-]$(M)	k' (s^{-1})
13	4.29e-5	8.08e-5	3.77e-3
14	4.29e-5	1.62e-4	6.82e-3
15	4.29e-5	2.42e-4	1.06e-2

Figure 12
ln Keq vs. 1/T, for FNCA

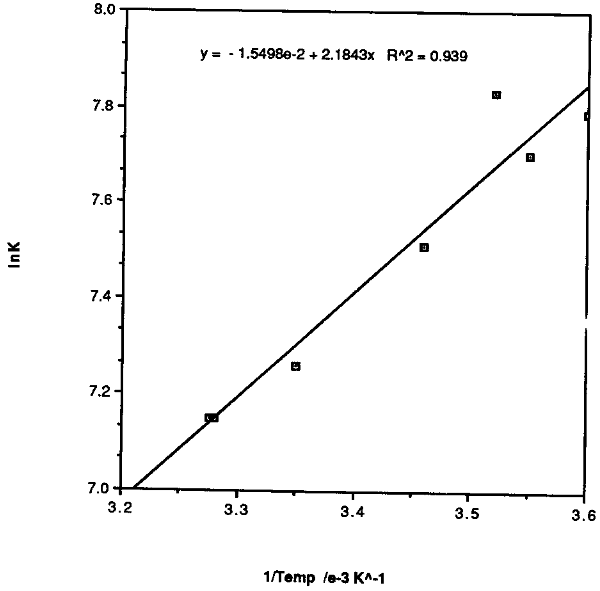


Figure 13 ln(A-Ainf) vs. Time, for FNCA
[HSO3-]=8.08 e-5 M

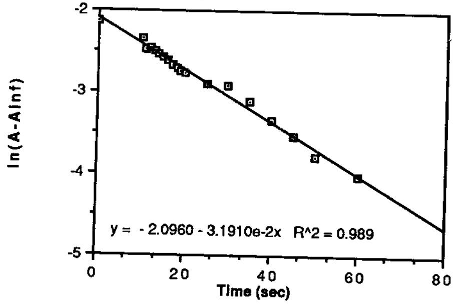


Figure 14 ln(A-Ainf) vs. Time, for FNCA
[HSO3-]=1.62 e-4 M

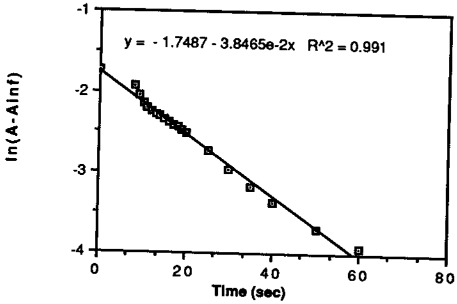
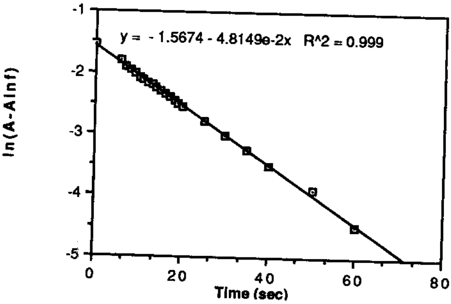
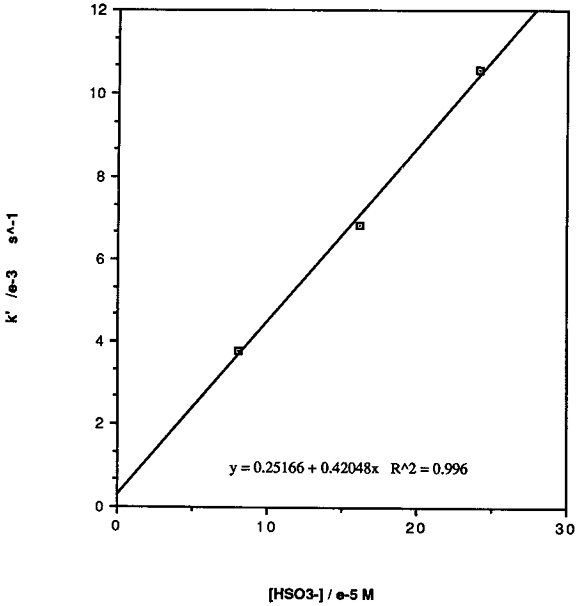


Figure 15 ln(A-Ainf) vs. Time, for FNCA
[HSO3-] = 2.42 e-4 M



The values of k' were plotted against the bisulfite concentration in Figure 16. From the slope of this graph, the forward rate constant for bisulfite addition to FNCA, was determined to be 42 $M^{-1}s^{-1}$. By calculation, a value of [illegible].1 X $10^{-2}s^{-1}$ was found for the reverse rate constant.

Figure 16
k1' vs [HSO3-], for FNCA



DISCUSSION

The kinetic and thermodynamic properties determined for bisulfite addition to the trans-cinnamaldehyde derivatives are presented, along with results obtained in LeTarte's study of trans-cinnamaldehyde (13), in Table 8. As a basis for comparison, an equilibrium constant for trans-cinnamaldehyde was determined in this study. The value obtained was 1100 M^{-1}, which was close to LeTarte's value of 1030 M^{-1}. It was concluded that results from the two studies would be comparable, and since LeTarte's value was an average of three runs, it was accepted as the true value. LeTarte's forward rate constant was recalculated using her data to replot k' vs. [HSO_3^-] for trans-cinnamaldehyde, this time excluding the (0,0) point.

Table 8 Summary of Results

	trans-cinnamaldehyde	DMACA	FNCA
wavelength of maximum abs.	291	399	308
extinction coefficient in buffer	25,400	26,000	23,190
K_{eq}/M^{-1}	1030	299 ± 7	1340 ± 90
$\Delta H^{\circ}/KJmol^{-1}$	-38	-39 ± 1	-18 ± 3
$\Delta S^{\circ}/Jmol^{-1}K^{-1}$	-71	-84 ± 3	-.1 ± 9
$k_1/M^{-1}s^{-1}$	25 ± 2	4.0 ± .3	42 ± 5
k_{-1}/s^{-1}	2.4 ± .2 e-2	1.3 ± .1 e-2	3.1 ± .4 e-2

Error values have been assigned to the results in Table 8. It is estimated that the minimum error in results obtained by this experimental procedure is 3.5%, and is due to error in the initial carbonyl concentrations. The error in the equilibrium constants is estimated by taking the greatest difference between values obtained, and dividing by two. The error in the entropy and enthalpy values is calculated by drawing high and low lines through the data points and using the equations of these lines to calculate high and low values. The range from the low value to the high value, divided by two, gives the error associated with the measured value. The error in ΔH° and ΔS° for bisulfite addition to FNCA is thus estimated. It should be noted that the error in this particular case is probably overestimated since the error analysis weighs heavily one point which is clearly out of line with the others (see Figure 12; note the fifth data point). Since the DMACA data plotted in Figure 4, ln K_{eq} vs. 1/T, yields a line with a correlation coefficient of 1.00, the error in ΔH° and ΔS° for DMACA is estimated to be just 3.5% (the error due limitations in the accuracy of aldehyde concentrations).

The error in the forward rate constants is estimated by drawing high and low lines through the data points as described above. Figures 8 and 16 show the data points, for DMACA and FNCA respectively, with a linear least squares fit. Theoretically, the intercepts of both plots should be zero. It is found that the intercept for the k' vs. [HSO_3^-] plot for FNCA does go to zero, within the limits of experimental error. The intercept for the k' vs. [HSO_3^-] plot for DMACA does not go to zero within the limits of experimental error. The intercept given by the least squares fit is 1.2580 e-3, and the low value is estimated to be 8.7992 e-4. This is an important observation because it indicates that there is some fast reaction, other than bisulfite addition, occurring which involves some species present in low concentration. It is hypothesized that this fast reaction may involve the SO_3^{2-} ion. Also, evidence for this fast reaction is not observed in data for trans-cinnamaldehyde or FNCA because the rates of bisulfite addition to these compounds are much faster than the rate for DMACA.

The electronic effect of the substituent on 4-dimethylaminocinnamaldehyde has two components- an inductive and a resonance component. The resonance effect of the $-N(CH_3)_2$ group is electron donating due to the fact that the p-orbitals of N are filled. The group is also inductively electron withdrawing. However, the group is electron donating overall by virtue of its overwhelming electron donating resonance effect. The result of the added electron density near the carbonyl carbon is the decrease in its ability to accept the negative bisulfite ion. Thus a decrease in the equilibrium constant and rate constant for bisulfite addition to 4-dimethylaminocinnamaldehyde (relative to trans-cinnamaldehyde) was observed.

The substituent on 4-nitrocinnamaldehyde is electron withdrawing both by inductance and resonance. The partial positive charge on N makes it inductively electron withdrawing, and the empty p-orbitals of N make $-NO_2$ potentially electron withdrawing by resonance. The electron withdrawing substituent facilitates the bisulfite addition by causing the carbonyl carbon to be more electron deficient (relative to the carbonyl carbon in trans-cinnamaldehyde), thus better enabling it to accept the negative bisulfite ion. There is therefore an observed increase in both the rate of bisulfite addition to 4-nitrocinnamaldehyde, and the corresponding equilibrium constant (relative to the reaction with trans-cinnamaldehyde).

The trend in rates and equilibrium constants discussed above is the same as that found by Young and Jencks (12) in their study of substituted acetophenones. In both studies, the results reflect the trends predicted by the

Hammett sigma constants for the substituents. These constants were developed to assess a given substituent's electronic effect on the ionization of substituted benzoic acids. The substiuent effects observed in the ionization of benzoic acids can be used to calculate effects of the same substituents on the bisulfite addition reaction. Of course a study of additional trans-cinnamaldehyde derivatives must be made before any quantitative comparisons can be drawn between the two reactions. However, since the reactions are similar (involving aromatic systems of about the same size, and a reaction that depends on a carbonyl carbon's ability to accept a negative charge) the effects of substituents should be similar. Hammett sigma values are negative for electron donating substituents, and positive for electron withdrawing substituents, while H (corresponding to the unsubstituted compound) is assigned a sigma value of zero. The following sigma values (corrected for possible solvent effects) are listed for the para substituents used in this study: -0.44 for $N(CH_3)_2$ and +0.82 for NO_2 (15). Thus, the trend in substituent effects observed so far is in accord with predictions based on Hammett sigma values.

The evidence so far indicates that the first step in the mechanism for bisulfite addition to a carbonyl compound is indeed the acceptance of the negative ion and not hydrogen ion addition (which comes later). If the hydrogen was added before the sulfite ion, we would expect the trend in equilibrium and rate values to be opposite of that which was observed.

The results in Table 8 also give an indication of the relative sensitivity of the measurements made. Notice that the forward rate constant appears to be a more sensitive measure of the substituents' electronic effects than the equilibrium constant. There is only a fourfold increase in the equilibrium constant from 4-dimethylaminocinnamaldehyde to 4-nitrocinnamaldehyde. Meanwhile, the rate constant increases by a factor of ten from the former derivative to the latter.

At this time, it is appropriate to consider whether significant amounts of bisulfite are actually tied up as adducts with the compounds used in this study. The equilibrium constant for the addition of bisulfite to an aldehyde is defined as:

$$K_{eq} = [\text{adduct}] / \{[\text{bisulfite}]\ [\text{aldehyde}]\}.$$

This relationship can also be expressed as:

$$[\text{Bisulfite}] / [\text{adduct}] \ = \ 1 / \{K_{eq}\ [\text{aldehyde}]\}$$

The ratio on the left side of the last equation is a measure of what fraction of bisulfite present in the atmosphere exists as an adduct, and what fraction is free bisulfite (known to be quickly oxidized to S(VI) in the presence of H_2O_2). Unless the bisulfite tied up as adduct is greater than 10% of the total bisulfite concentration, it can be said that the extent of formation of that adduct is insignificant.

Assuming aldehyde concentrations are on the order of 2×10^{-6} M (which is reasonable for formaldehyde, but concentrations of other aldehydes are lower), a range of equilibrium constants can be substituted into the equation above to determine at what value of equilibrium constant, adduct formation becomes significant. Table 9 shows the results of such calculations.

Table 9 Theoretical Calculation of Amounts of Bisulfite Tied Up as Adduct for Given K_{eq} Values (assume [aldehyde] is 2 X 10^{-6} M)

K_{eq}	[bisulfite]/[adduct]	% bisulfite in the form of adduct
85,000	6:1	~14%
60,000	8:1	~11%
15,000	33:1	<3%
1,000	500:1	<0.2%
100	5,000:1	<0.01%

The results in Table 9 suggest that bisulfite addition to aldehydes with an equilibrium constant less than 60,000 M^{-1} is insignificant. Formaldehyde has been reported to have an equilibrium constant of 85,000 M^{-1} (10), and 4,000,000 M^{-1} (16). In either case, it seems that adduct formation with bisulfite and formaldehyde is important to the overall scheme of cloudwater chemistry. However, acetaldehyde has the next highest equilibrium constant, reported to be 16,000 M^{-1} (17). From Table 9, it is clear that even at the overestimated aldehyde concentration, bisulfite addition to acetaldehyde could only take up less than 3% of the bisulfite in the atmosphere. Unless acetaldehyde concentrations are approximately 7 X 10^{-6} M, formation of the acetaldehyde-bisulfite adduct is not a significant process in cloudwater chemistry. Trans-cinnamaldehyde and its derivatives have equilibrium constants on the order of 100 - 1,000 M^{-1}. It is extremely unlikely (assuming their presence) that significant amounts of bisulfite adducts will form with these aldehydes in cloudwater.

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$[DMACA]_0 = 3.46 \times 10^{-5}$ M „ buffer

T = 0.5°C

pH = 4.6

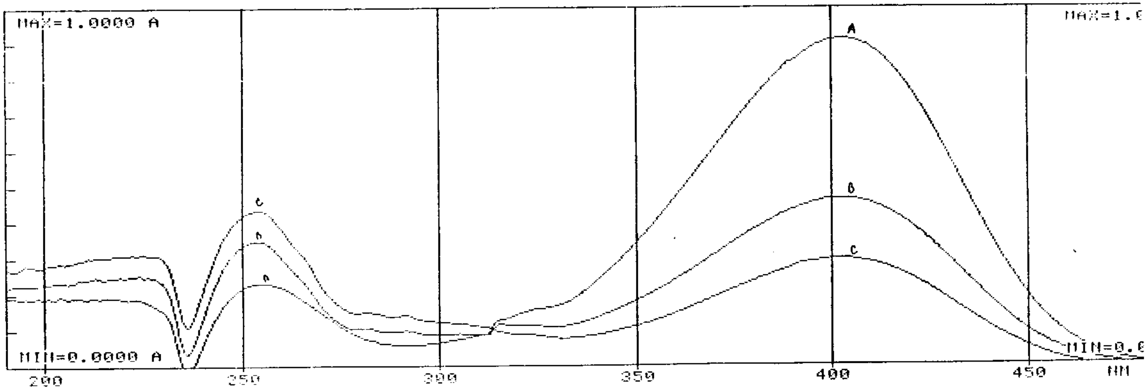
A $[HSO_3^-]$ = 0

B $[HSO_3^-]$ = 8.08×10^{-4} M

C $[HSO_3^-]$ = 1.62×10^{-3} M

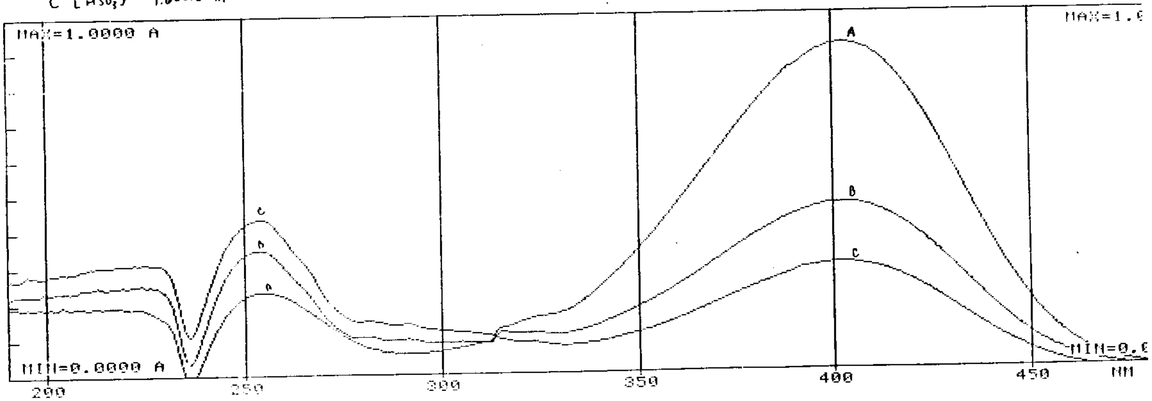
Abs. vs. λ

[illegible]



$[DMACA]_0 = 3.46\times10^{5}$ M in buffer
T = 0.5°C
pH = 4.0
A $[HSO_3^-]$ = 0
B $[HSO_3^-]$ = 8.08×10^{-4} M
C $[HSO_3^-]$ = 1.62×10^{-3} M

Abs. vs. λ



4-nitrocinnamaldehyde in buffer

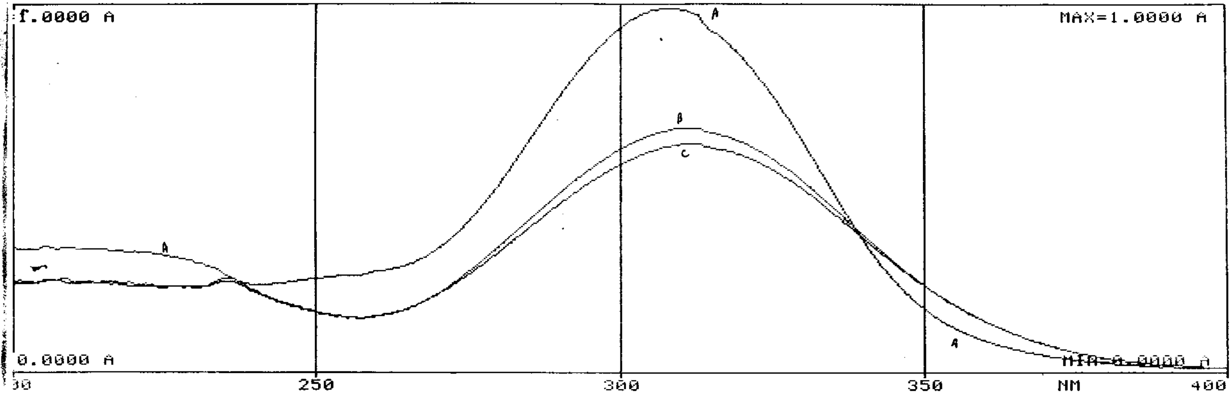
$[FNCA]_0 = 4.24 \times 10^{-5}$ M

T = 25°C pH = 4.63

$[HSO_3^-] = 0$ for A

8.08×10^{-4} M for B

1.62×10^{-3} M for C



Absorbance vs time